# GASEOUS PRECISION ETCHING OF MOLYBDENUM

By: RUTH C. PREIST

*Prepared for:*

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INFORMATION SYSTEMS BRANCH
DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH
WASHINGTON, D.C. 20360

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STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA ✳SRI

*Technical Report*

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Copy No. 38

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ILLUSTRATIONS

# I INTRODUCTION

The object of the work described in this report has been to explore
the possibilities of etching thin films of molybdenum or aluminum oxide
using gaseous rather than liquid reagents. The most immediately obvious
advantage in the use of gases at low pressures, instead of liquids, was
that etching could be accomplished in the same equipment as that used
for other steps in fabricating thin-film devices in high vacuum, or similar
equipment. The goal was to develop a process capable of producing patterns
having dimensions with resolution better than a micron in films 1/2 to
2 microns thick.

One approach to chemical etching with gases--the method which is the
subject of this report--is to use a gas or a combination of gases which
will react with the molybdenum or aluminum oxide to form a volatile com-
pound which can be made to evaporate, leaving a clean, smooth, and un-
damaged surface behind. Some of the effects which, if characteristic of
a process, would destroy the usefulness of that process are: residues
of nonvolatile by-products of the reaction left on the surface; selective
attack at grain boundaries or dislocations; destruction of the resist
layer; or damage to the adjacent structures or underlying layers.

Since quite a lot of work has been previously done on gaseous etching
of $Al_2O_3$[1,2]* in vacuum, efforts were concentrated on etching metallic
molybdenum films.

Since good control of depth and degree of undercutting was important,
electron micrographs were taken of any etched structures that appeared
promising under the optical microscope.

Most of the effort was concentrated on perfecting the reaction
between a heated molybdenum surface and a mixture of oxygen and hydrogen
chloride gases to form the volatile molybdenum oxychloride. A few tests
were made using pure chlorine, carbon tetrachloride vapor, and pure oxygen.

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*References are listed at the end of this report.

Other material describing this work is contained in Quarterly Progress Reports Nos. 3 and 4, Contract Nonr-3449(00) and in Combined Quarterly Status Reports Nos. 19, 20, 21, and 22, Contracts Nonr-2887(00) and Nonr-3449(00).
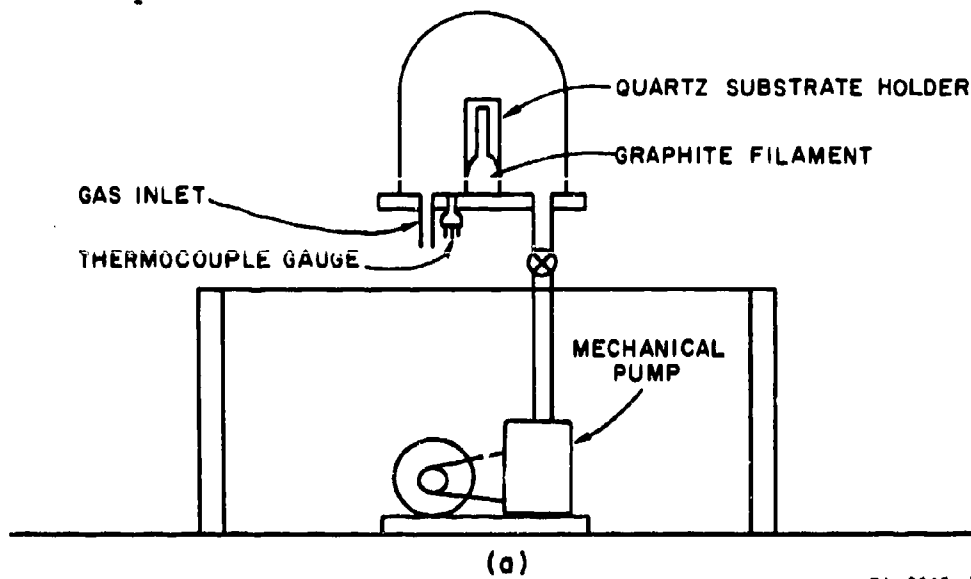
## II APPARATUS

In order to avoid possible damage to the oil-diffusion pumps, valves, etc., in the standard high-vacuum stations by HCl or other corrosive gases, a separate vacuum station shown in Fig. 1(a) was assembled. The new station had the advantages that the radiant heater was isolated from the reaction chamber by a quartz sleeve, and that the substrate surface could be closely observed during the etching process.
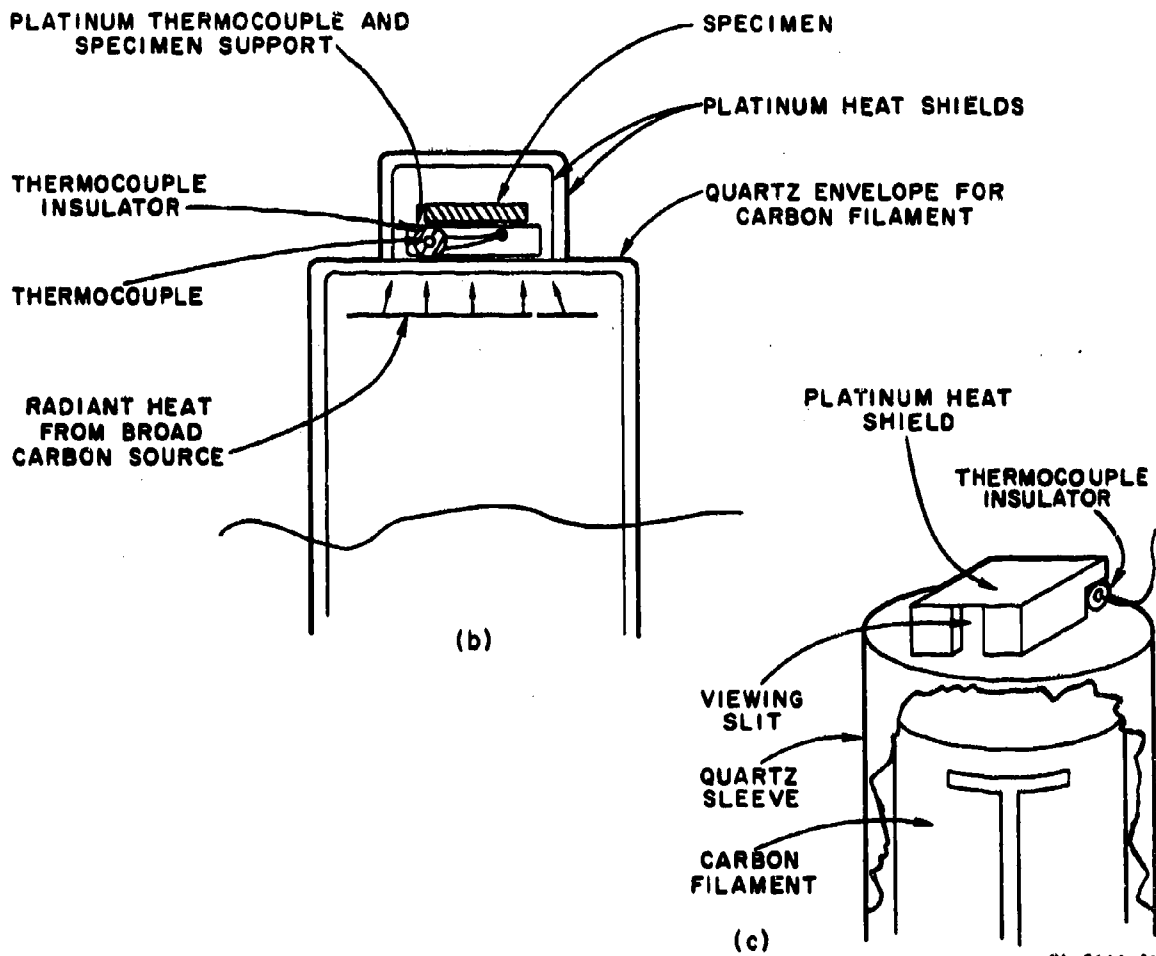
The limitations of this arrangement, however, were that measurements of gas pressure and substrate temperature were difficult and dubious. Also, the background pressure and pumping speed obtained from the mechanical pump were not comparable to those obtainable in a high-vacuum station.

The problem of substrate temperature measurement was solved at the expense of loss in visibility of the substrate during etching, by enclosing the substrate along with a thermocouple in a platinum box. The position of the thermocouple was modified until thermocouple readings were within 10° at 1000°C of optical pyrometer measurements made on carbon coated sample specimens. This is shown in Figs. 1(b) and 1(c).

The gas-handling arrangement is shown in Fig. 2. The same method of control and measurement was used for both HCl and $O_2$ gases. The flow meter was isolated from the high-pressure supply by a pressure regulator and from the vacuum chamber by a needle-type metering valve. Two one-liter gas volumes were used to reduce fluctuations in pressure at the flow meter. However, even with the use of the gas-ballast tanks, fluctuations caused by opening and closing of the automatic pressure regulators caused erroneous flow-meter readings. To avoid the effect of these small variations on the flow-rate readings, the flow meters were calibrated and readings were taken only with the inlet valve to the first ballast tank closed, so that the flow of gas through the flow meter was a function only of the pressure in the first ballast tank and of the rate of gas flow through the metering valve. The fall in pressure in the first ballast tank during the time required to read the flow meters was negligible.

QUARTZ SUBSTRATE HOLDER

GRAPHITE FILAMENT

GAS INLET

THERMOCOUPLE GAUGE

MECHANICAL PUMP

(a)

TA-2863-1

PLATINUM THERMOCOUPLE AND SPECIMEN SUPPORT

SPECIMEN

PLATINUM HEAT SHIELDS

THERMOCOUPLE INSULATOR

QUARTZ ENVELOPE FOR CARBON FILAMENT

THERMOCOUPLE

RADIANT HEAT FROM BROAD CARBON SOURCE

(b)

PLATINUM HEAT SHIELD

THERMOCOUPLE INSULATOR

VIEWING SLIT

QUARTZ SLEEVE

CARBON FILAMENT

(c)

TA-8444-80R

FIG. 1   VACUUM STATION
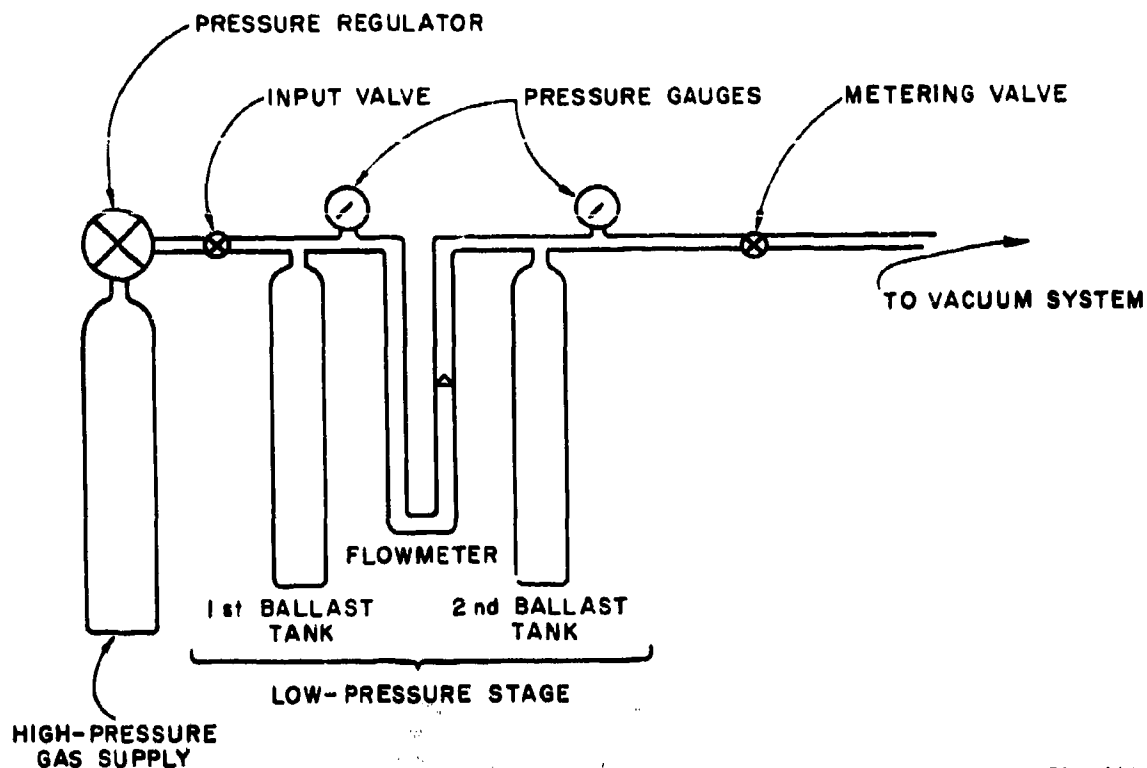
FIG. 2  GAS-HANDLING APPARATUS

Figure 3 is a calibration curve for both the $O_2$ and HCl flow meters. Also shown is the change in pressure in the bell jar (as indicated by the thermocouple gauge) as a function of the rate of gas flow into the bell jar.

The change in pressure as indicated by the thermocouple gauge for a given amount of gas input is, of course, a function of changes in pumping speed for different gases and pressures, of valve and pump conditions, and also of differences in thermocouple-gauge sensitivity for different gases.

Because of the insensitivity of the thermocouple gauge to changes in pressure of HCl gas, which is quite evident from the calibration curve, some other type of gauge should have been used.
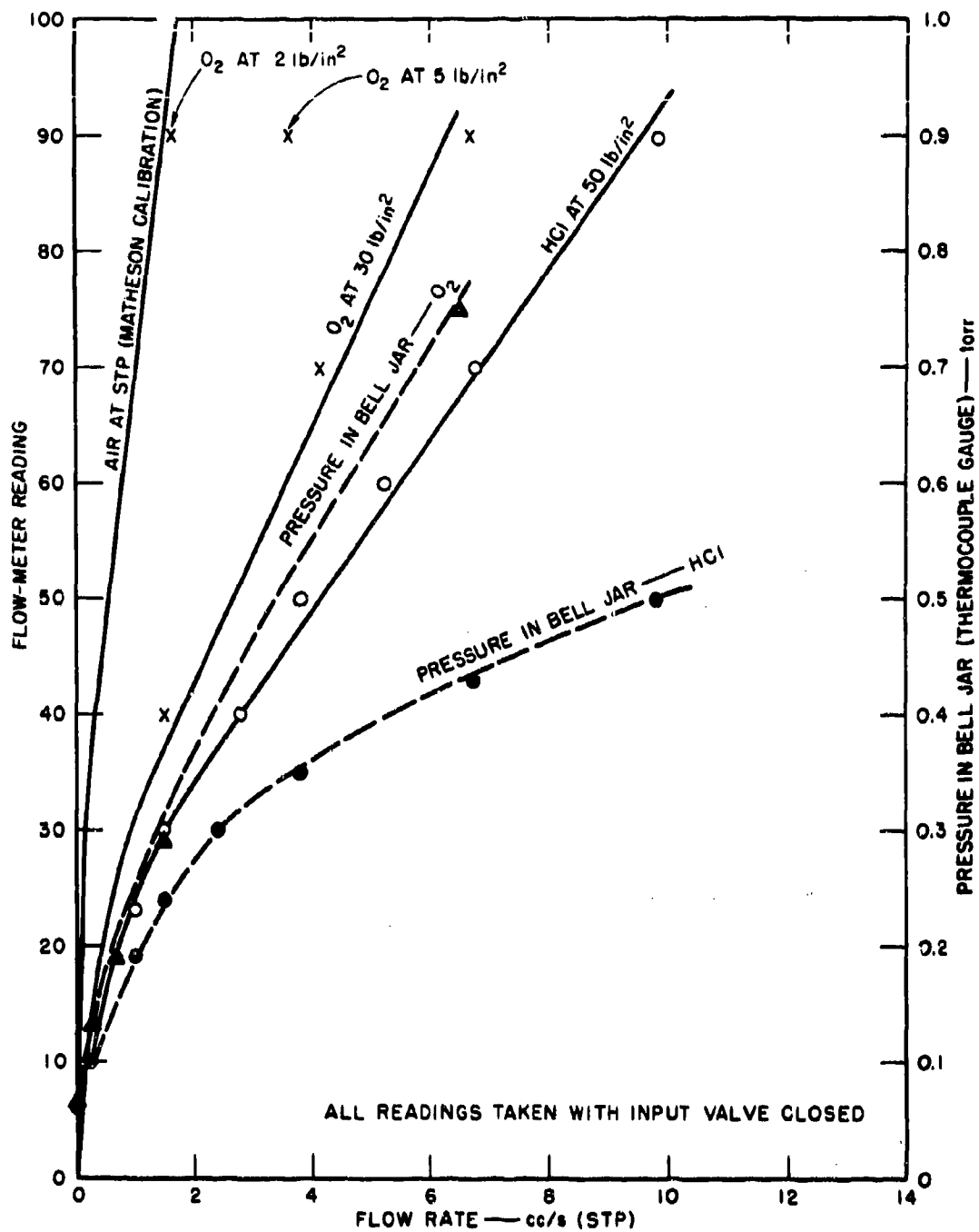
FIG. 3 CALIBRATION CURVES FOR FLOW METERS

FLOW-METER READING

PRESSURE IN BELL JAR (THERMOCOUPLE GAUGE) — torr

FLOW RATE — cc/s (STP)

$O_2$ AT 2 lb/in²

$O_2$ AT 5 lb/in²

$O_2$ AT 30 lb/in²

AIR AT STP (MATHESON CALIBRATION)

HCl AT 50 lb/in²

PRESSURE IN BELL JAR

$O_2$

HCl

PRESSURE IN BELL JAR

ALL READINGS TAKEN WITH INPUT VALVE CLOSED

TB-2863-2

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A useful feature of the gas-handling system described above is that the sensitivity or range of the flow meters can be changed by changing the pressure in the first ballast tank. This is often helpful, since it is difficult to predict ahead of time what size of flow meter may be required for a particular application. Ordinarily, several flow meters would have been required to cover the range of gas flow rates shown in Fig. 3.

III  METHODS

Two types of specimen were used in the course of the experiments.
The first used were 1/2-inch squares of Corning Type 7059 glass about
0.030 inch thick. The glass is described as a barium aluminum borosili-
cate composition with a softening point of 835°C. The surface finish
was as drawn or fusion-formed, without grinding or polishing. Polished
sapphire substrates of about 3/16 X 1/4 inch were also used.

The substrates were cleaned and coated with molybdenum by evaporation
in vacuum from an electron-bombardment heated source. Films from 1/2 to
over 1μ thick were laid down at rates of roughly 1 to 4 μ/hour. $Al_2O_3$,
put on in the same manner as the molybdenum, was used as the resist.
When patterns in the resist were required, polystyrene balls of 1/2 to
1μ diameter* were blown from a nebulizer over the molybdenum surface and
the $Al_2O_3$ was deposited over them. The balls could easily be removed by
a short ultrasonic cleaning in detergent and water, leaving neat holes
in the resist with diameters slightly larger than the diameter of the
polystyrene spheres. Most of the early work was done using the 1/2-inch
square substrates fully coated with molybdenum, without resist. In the
exploratory stages, the temperature was made considerably higher at the
center of the substrate, with a sharp decrease toward the edge, in order
to see the effects of temperature variations under a uniform condition
of gas mixture and pressure.

Experiments designed to relate etching conditions to such factors
as degree of undercutting were done with the specimen placed inside the
platinum box. The temperature was uniform over the specimen surface and
could be controlled and measured to within ± 10°C. It was, however, some-
what difficult to determine the end of etching because of limited visibility.

The etched specimens were inspected under transmitted and reflected
light with the Reichert metallographic microscope. Specimens were

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*Obtained from Bioproducts Department (Mr. L. G. Lipple), Dow Chemical
 Company, P.O. Box 512, Midland, Michigan  48641.

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replicated for observation in the electron microscope, and a few examples of microphotographs are included in this report. Both straight-on and side views of the carbon replicas of holes are shown.

The gas flow meters were calibrated by allowing the gas to flow into a measured volume at a constant (atmospheric) pressure.

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## IV  SUMMARY OF RESULTS

In the initial work on this topic, the etching of molybdenum with pure oxygen gas by the formation of molybdenum trioxide was attempted. Since sublimation of $MoO_3$ in air starts at $610^\circ$ to $650^\circ C$ it was hoped that reasonable etching rates could be achieved at $600^\circ$ to $700^\circ C$ in a vacuum with a partial pressure of oxygen of less than $10^{-4}$ torr. However, it was found that the reaction was very slow up to $850^\circ C$ and a heavy residue of semitransparent material was always noticeable on the etched surfaces. Experiments with monoatomic oxygen produced by the decomposition of manganese dioxide also failed to yield sufficiently rapid etching rates.

Later, molybdenum films were exposed to pure $O_2$ at much higher pressures and etching rates of 500 to 700 Å/min were obtained at about $700^\circ C$ and an $O_2$ pressure of 0.5 to 1 torr. A thick residue was still easily seen on the surface of the substrate, however. Some other gases and combination of gases were tried, and a short summary of the results is given at the end of this report. The most interesting of these results were that pure HCl did not etch at all, and that pure chlorine gas etched molybdenum very rapidly, but a thick residue was left on the exposed surfaces of molybdenum and the etched patterns were irregular and severely undercut.

When a combination of oxygen and hydrogen chloride gases was tried at pressures of 0.3 to 0.6 torr and with substrate temperatures of about $500^\circ$ to $700^\circ C$, good etching rates and some better-than-average etch patterns were obtained. Because of the relatively high pressures required for etching, attempts at collimation of the molecular beam, a technique which we hoped would reduce undercutting at the edge of the resist, were abandoned rather early; but the otherwise favorable results encouraged more exploration of this process. Final results can be summarized as follows:

(1) A given set of etching conditions—i.e., temperature, time, pressure, and gas mixture—can now be repeated with reasonable accuracy to produce etched holes of the type shown in the micrographs in Fig. 4.

(2) A film of $MoO_2$ is usually present on molybdenum surfaces which have been exposed during etching. If all the molybdenum is removed, the film of $MoO_2$ is also removed, since it is one of the steps in the overall reaction. Methods of removing this film are discussed in another section of this report.

(3) The degree of undercutting and the hole shape can be controlled to some extent by varying the gas mixture and the substrate temperature. The etch factor, (which is defined as the ratio of the depth of etch divided by the distance etched under the edge of a resist) has been about 2.

(4) The presence of an oxide layer during etching is an important characteristic of this particular process; it contributes to a smoothing action and is important in determining the rate of etching as a function of surface contours. For example, a 1.5-mil molybdenum wire with a temperature gradient along its length was etched in order to learn whether this process would tend to attack grain boundaries, or etch certain crystal faces preferentially. Instead, the wire diameter was reduced smoothly and uniformly from its original value (about 38µ) to about 4µ. This is seen in Fig. 5, in which four sections of the wire, representing successively higher etching temperatures, are shown.

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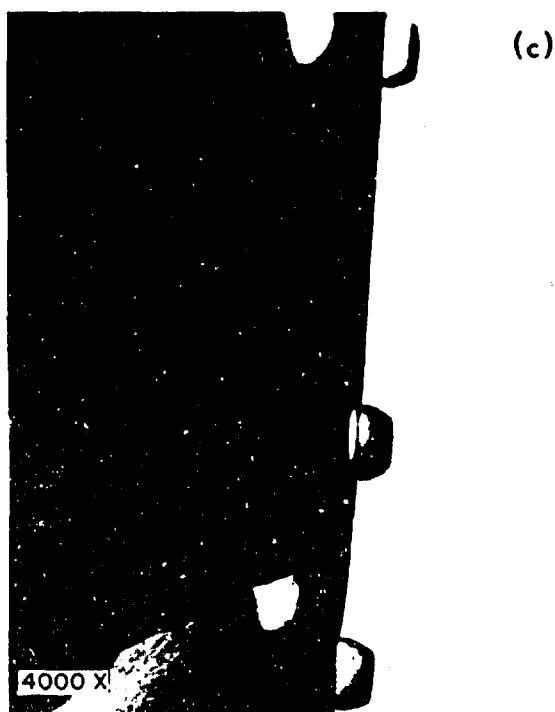
FIG. 4   MICROGRAPHS OF  TYPICAL  HOLES (a-d) Sample No. 45, Batch 6 substrate,
4500Å thick molybdenum, 1/4μ balls 670°C, 17 min, 3.8 cc/s $O_2$, 0.2 cc/s HCl
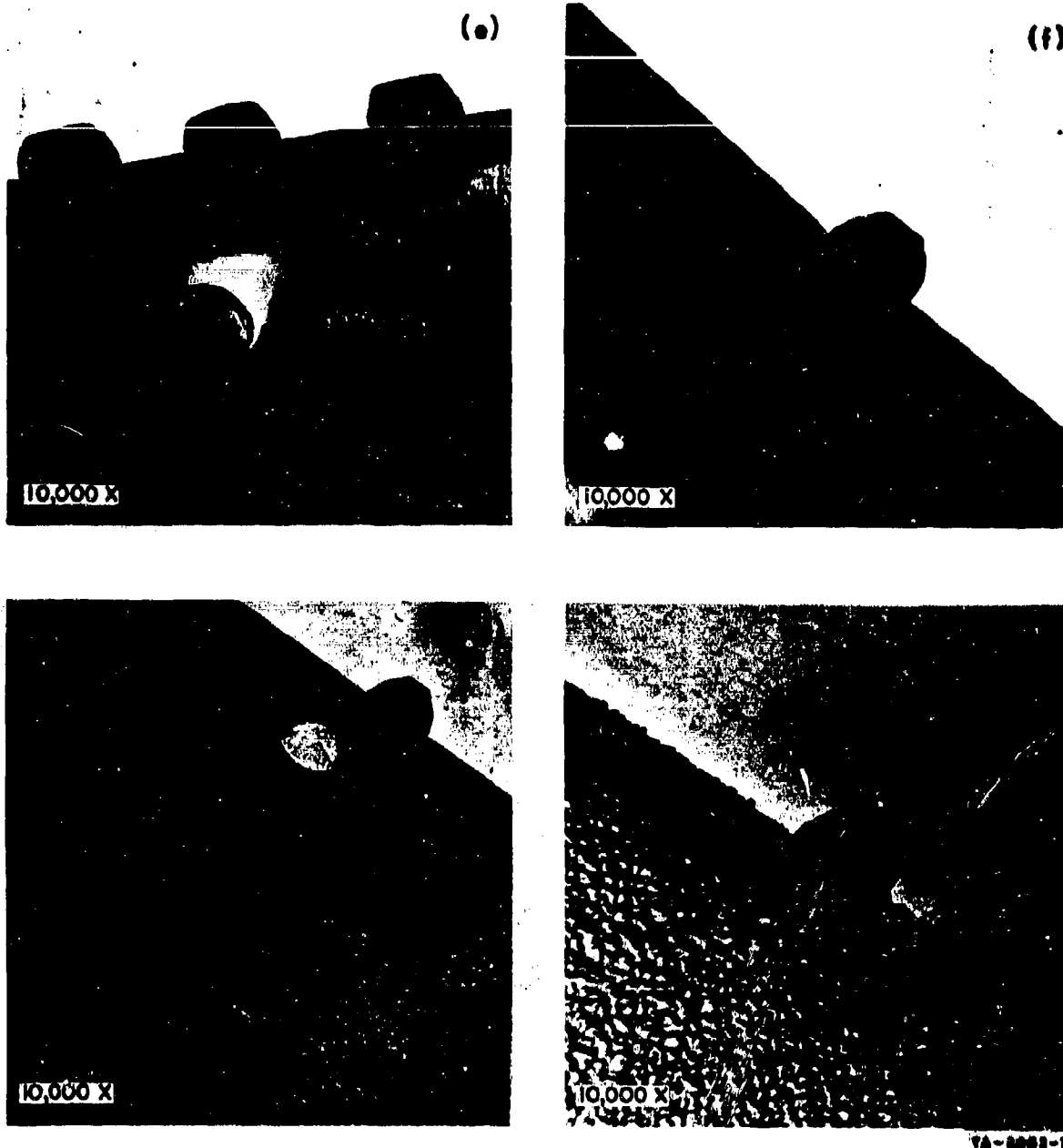
12

FIG. 4 (Continued) MICROGRAPHS OF TYPICAL HOLES (e) Sample No. 45, Batch 6 substrate 670°C, 17 min, 3.8 cc/s $O_2$, 0.2 cc/s HCl (f) Sample No. 47, Batch 6 substrate 670°C, 10 min, 7.8 cc/s $O_2$, 0.2 cc/s HCl (g) Sample No. 49, Batch 6 substrate 670°C, 22 min, 3.8 cc/s $O_2$, 0.1 cc/s HCl (h) Sample No. 56, Batch 7 substrate 670°C, 10 min, 7.8 cc/s $O_2$, 0.2 cc/s HCl

(a) 36μ DIAMETER (UNETCHED)

(b) ETCHED TO ABOUT 23μ, WITH BARELY VISIBLE SHEATH

(c) ETCHED TO ABOUT 10μ, SHOWING TRANSPARENT SHEATH

(d) ETCHED TO ABOUT 4μ, SHOWING TRANSPARENT SHEATH

TA-5444-36

FIG. 5 EFFECT OF LONGITUDINAL TEMPERATURE GRADIENT ON MOLYBDENUM WIRE DURING ETCHING

(5) Etching rates of 100 to 6000 Å/min have been measured for substrate temperatures of 480°, 580°, and 670° C, and pressures in the bell jar of roughly 0.4 to 1 torr. The rate of etching appears to increase with increased amounts of either HCl or $O_2$ admitted to the reaction chamber over a wide range of gas mixtures.

(6) Lack of corrosive or selective attack of surfaces, the possibility of control of the etch factor, uniformity in hole shape and size, and relatively easy control of etching conditions seem to be the outstanding characteristics of this process.

(7) Vacuum-deposited films of $Al_2O_3$ of 1500Å or more in thickness have been impervious to the etchant gases up to 800° C.

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## V  DISCUSSION

### A.  Chemical Background

It is assumed that the removal of molybdenum by oxygen and hydrogen chloride gases is accomplished by the formation of $MoO_2Cl_2$ by two reactions:[3,4]

$$2Mo + 3O_2 \rightarrow 2MoO_3$$

and

$$MoO_3 + 2HCl \rightarrow MoO_2Cl_2 \cdot H_2O \qquad .$$
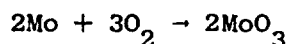
Molybdenum oxychloride is volatile at $200^\circ$C and a gas at about $300^\circ$C. It is formed at temperatures of $150^\circ$ to $300^\circ$C or higher by the reaction given above.

The rate of etching at low temperatures seems to be limited by the rate of formation of $MoO_3$, which is observed to be very slow at $400^\circ$C and quite fast at $600^\circ$C.[5,6,7]  Since we would like to etch at the lowest possible temperatures, and since the oxychloride is easily formed at relatively low temperatures, it is of some interest to consider the factors which ultimately limit the rate of reaction between oxygen and molybdenum at temperatures around $300^\circ$ to $400^\circ$C.

We are concerned with the structure of the oxide layer as well as the rate of formation of the oxide, since there is some basis for regarding the oxide layer as important in achieving the desired etch factor and a smooth etched surface and since it constitutes a problem in its removal at the end of etching.

It is important to point out that in any high-temperature reaction between a metal and a gas, only rarely is the reaction zone limited to to the top molecular layer of the metal.  Unless the reaction products are volatile, they will remain as a boundary layer between the gas and the metal and will determine the course of the reaction thereafter.

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Even if one reaction product is removed as fast as it forms, other reactions can, and often do, take place.

In the normal oxidation of molybdenum the growth of the oxide film, at least when it is thin and the temperature is below 600° to 700°C, has been shown to occur almost entirely by the diffusion of oxygen from the surface inward.[8]  Molybdenum is known to have at least two oxidation states:  $MoO_3$ and $MoO_2$, and when molybdenum is oxidized at temperatures under 770°C these are arranged with $MoO_3$ at the solid-gas interface and the $MoO_2$ (and possibly some intermediate oxides) nearest the metal. Oxygen is known to be soluble in the metal also.

The relative thickness of the layers of $MoO_3$ and $MoO_2$ and the amount of dissolved oxygen depends upon the relative rates of the dissociation reactions:

$$MoO_3 \rightleftharpoons MoO_2 + O$$

$$MoO_2 \rightleftharpoons Mo + 2O \qquad ,$$
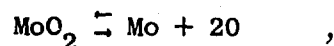
and on the solubilities and diffusion rates of oxygen in the various layers, as well as on the rate of the absorption of, or reaction of, oxygen atoms at the surface of the $MoO_3$.  All of these factors are temperature-dependent.

In order to develop a tangible picture, we can suppose that after the first molecular layer of $MoO_3$ is formed, further transport of oxygen into the metal must take place either by the dissociation of $MoO_3$ with subsequent diffusion of the oxygen atoms inward, or by interstitial or vacancy-site diffusion of oxygen through the $MoO_3$ layer.  Since $MoO_3$ is known as a metal-excess semiconductor, the former process is more likely.[8,9]

It may be seen by this line of thought that the oxidation of molybdenum must be regarded both in terms of chemical reactions and in terms of other rate-determining processes such as the absorption, diffusion, and desorption of gases in solids.

B.    Possible Effects of Using Atomic or Ionized Oxygen

In the oxidation of molybdenum, it is reasonable to expect an increase in the probability of reaction between molybdenum and atomic oxygen over that for diatomic oxygen for two reasons:  First, it is generally accepted that diatomic gases cannot diffuse through metals or crystalline materials (even though gases, in the diatomic or molecular form, do diffuse without dissociation through glasses).  Second, the energy of dissociation of diatomic gases must be available before a new chemical combination can take place.

An increase in oxidation probability of almost three orders of magnitude for atomic oxygen over diatomic oxygen has been reported[10,11] and copies of two published curves are shown in Figs. 6 and 7.  Even though the results shown in Fig. 6 were obtained at higher temperatures and lower pressures than the conditions which we contemplate using, the report offers us some encouragement for using atomic oxygen in order to achieve a higher rate of oxidation at lower temperatures than has otherwise been possible so far.  If by using atomic oxygen the temperature could be reduced to $300^{\circ}$ to $400^{\circ}C$ for the oxidation of molybdenum and the subsequent reaction with HCl, the problem of the diffusion of oxygen to form $MoO_2$ could be controlled, since the rate of diffusion is temperature-dependent, and the etch factor may be improved.  Also, at a temperature of $350^{\circ}C$, failure of the electron-sensitive resists should be less likely to occur.  It may be reasonable to expect the sticking probability of ionized oxygen to be even greater than that of atomic oxygen.[12]

The problem in using either atomic or ionized oxygen is to have a reasonably high portion of the gas in the active state.  Even though the probability of reaction is improved, the overall increase in the rate of reaction depends upon both the probability of reaction and the actual number, or partial pressure, of the active species present.

The use of slow electrons or radiant energy to help speed the process at the molybdenum surface may be of some use.
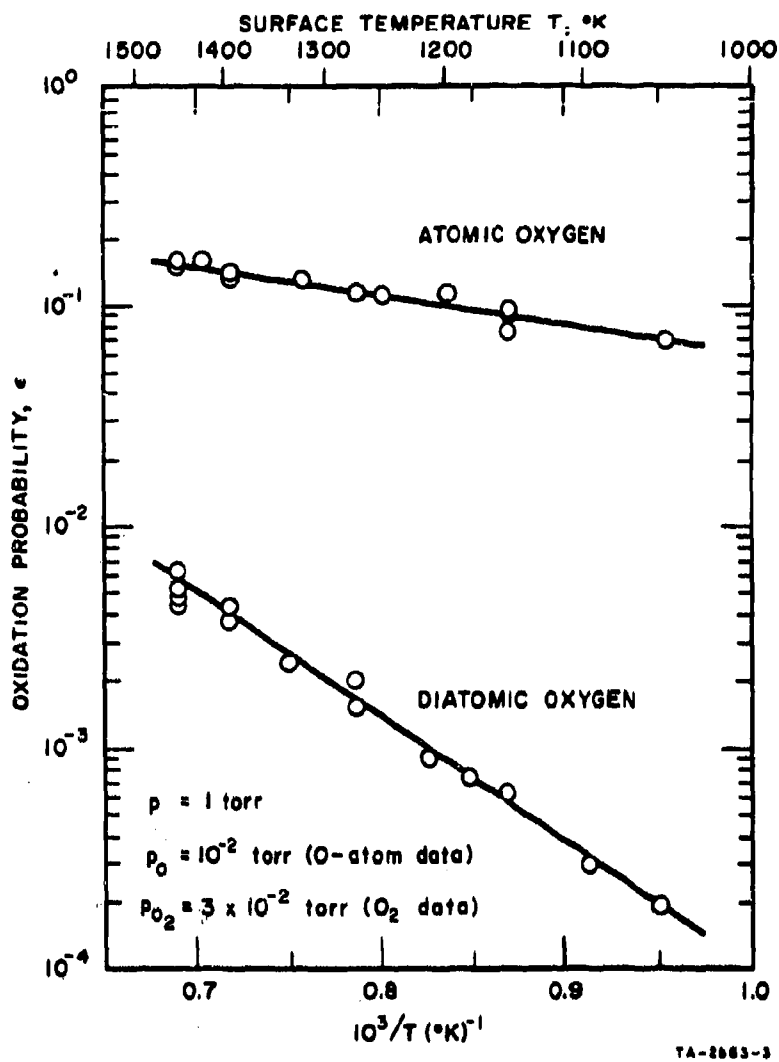
FIG. 6 ARRHENIUS PLOT OF MOLYBDENUM OXIDATION PROBABILITIES
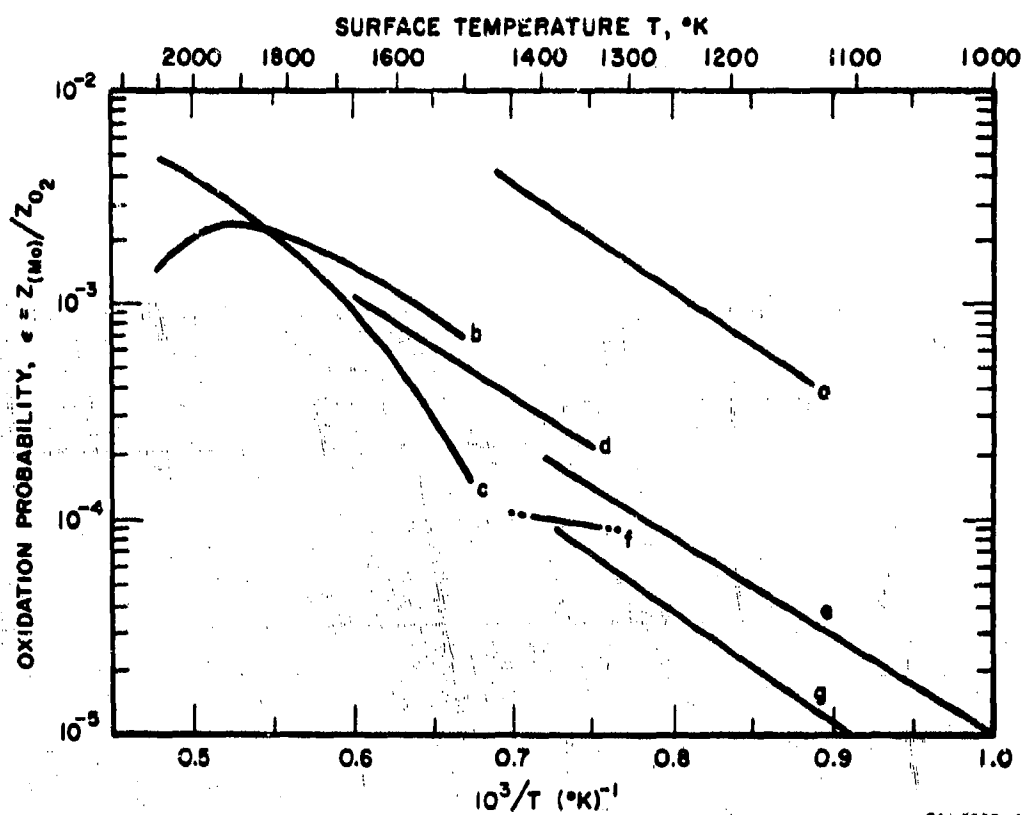FOR ATOMIC AND DIATOMIC OXYGEN

FIG. 7 ARRHENIUS PLOT OF MOLYBDENUM OXIDATION PROBABILITIES
FOR VARIOUS MEDIA

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## C.  Pressure Considerations

It is of some interest to try to predict the best vacuum conditions (i.e., the lowest pressures) and the smallest amounts of reagents required for a reasonable rate of etching, and also to compare the theoretical maximum efficiency with that achieved in practice.

The following computations are to determine the time and reagent required to etch a 1µ thick layer of molybdenum from an area of 1 $cm^2$ assuming bombardment of the surface to be etched by single atoms of reactive gas, no collisions between gas particles, and 100 percent efficiency of reaction.  The reaction between oxygen and molybdenum is used as an example, and it is assumed that the $MoO_3$ is removed by volatilization or some noninterfering reaction.

The amount of molybdenum to be reacted is:

$1 \times 10^{-4} cm^3$, or

$10.2 \times 10^{-4}$g, or about

$1 \times 10^{-5}$ mole.

If the molybdenum is to be removed by formation of $MoO_3$ and its subsequent volatilization by the reaction

$$Mo + 1\text{-}1/2 \ O_2 \rightarrow MoO_3 \quad ,$$
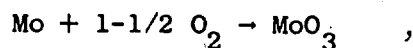
$1.5 \times 10^{-5}$ moles of $O_2$ or

$3 \times 10^{-5}$ moles of O will be required.

The volume of O used is approximately

$6.6 \times 10^{-4}$ liter at STP, (~0.6 cc) or about

$6 \times 10^4$ liter at $10^{-5}$ torr.

Merely in order to relate these quantities to existing equipment, we find that if this amount of gas is introduced into a typical bell jar with a pumping speed of about 200 liters/second (with no getter assist) in the pressure range of $10^{-6}$ to $10^{-5}$ torr, and it does not react to form

a low vapor pressure oxide, it will take roughly 5 minutes to remove the gas from the chamber if the pressure is held to $1 \times 10^{-5}$ torr or less; or if this amount of gas is admitted to a bell jar with a volume of 100 liters, and with a starting pressure of anything less than $10^{-5}$ torr, the final pressure with no pumping will be $6 \times 10^{-3}$ torr.

If, in the case of etching molybdenum, all the O reacted with Mo as soon as it landed, there would be only the pressure rise from the vapor pressure of the $MoO_3$ which is expected to be volatilized from the molybdenum surface and condensed on cold surfaces elsewhere. However, if some portion of the molybdenum surface is masked, as it would be in most practical situations, the O which strikes the masked areas will leave and will contribute to a pressure rise in the system.

If one assumes that in practice, in addition to the gas which is rejected from masked areas, only 10 percent of the gas introduced can be expected to contact the surface to be etched before it is pumped away, and that the reaction efficiency (i.e., the probability of absorption after collision with an active surface) is 10 percent, then the etching time becomes something approaching 500 minutes if the pressure is held to $1 \times 10^{-5}$ torr and limited by pumping speed.

If pumping speed is not a limiting factor, i.e., if all the gas atoms admitted to a system can be removed as fast as they leave the etching zone, the next limiting factor would seem to be the rate of impact of oxygen atoms on the surface to be etched as a function of the partial pressure of oxygen over that surface.

As a means of starting the discussion, if we again wish to maintain the equivalent of a vacuum of $1 \times 10^{-5}$ torr over the active surface,[*] we find that the volume of gas which strikes a unit area per unit time is given by:[13]

---

[*] This pressure range has been chosen because it is a favorable pressure at which one can make effective use of electron emitters, and where the probabilities of collisions between gaseous particles are such that reasonable lifetimes of dissociated atoms can be expected.

$$F = 3638 \left(\frac{T}{M}\right)^{1/2} cm^3 \cdot sec^{-1} \cdot cm^{-2}$$

$$= 3638 \left(\frac{700}{16}\right)^{1/2}$$

$$= 3638 \cdot 6.6$$

$$\approx 24 \text{ liter} \cdot sec^{-1} \cdot cm^{-2}$$

where T is assumed to be $700^\circ$K

and M = molecular weight of O.

We need $6 \times 10^4$ liters at $10^{-5}$ torr; and therefore it will take $2.6 \times 10^3$ seconds or about 45 minutes for a sufficient number of O atoms to arrive to form $MoO_3$ at $1 \times 10^{-5}$ torr pressure of O at $700^\circ$K. If the efficiency is less than perfect, because of collisions with $MoO_3$ molecules leaving the surface, or because of the collisions with impurity gases which might be present either in the gas over the surface or sticking on the surface, the time for etching may be extended again to 500 minutes.

From the above considerations, it would seem that in order to convert the $1\mu$ layer of molybdenum to $MoO_3$ in a reasonable time, that the arrival rate of O atoms must be equivalent to a partial pressure of O over the surface of at least $1 \times 10^{-4}$ torr, and this would require a high efficiency of all steps in the reaction.

If, in fact, the probability of oxidation at $1000^\circ$K with diatomic oxygen is around $1 \times 10^{-4}$ as reported and shown in Figs. 6 and 7, then the pressure for an etch rate of 0.1 to 1 $\mu$/minute using molecular oxygen will have to be about 0.1 to 1 torr. It is therefore not surprising that this is the pressure range which has been found to be required in our work so far.

In terms of total quantity of oxygen required to etch $1\mu$ of molybdenum, we find that under rapid etching conditions we used 3.8 cc $O_2$ (STP) per second for about 100 seconds, or a total of 380 cc. Compared with the theoretical requirement of 0.6 cc (STP) it appears that we used one molecule out of about $6 \times 10^2$ molecules admitted.

This is somewhat better than might be expected, if the probability of reaction is as low as indicated in Figs. 6 and 7. The explanation could be that some of the oxygen molecules impinged on the molybdenum surface many times before they were removed from the system. In an entirely closed system, for example, the efficiency of reagent use could be 100 percent, but the rate of the reaction would still be dependent upon the partial pressure of the oxygen present, which of course would diminish with time.

D.  Formation and Removal of the Oxide Film

A thin film of relatively hard, adherent, and transparent material can usually be seen on a partially etched molybdenum surface after a typical etching cycle using the oxychloride process. This film is usually pale brown, corresponding to a color thickness of 300 to 500Å. The film has been identified as $MoO_2$, a compound which is stable to about 1780°C when heated in bulk in vacuum. It is a fairly good conductor of electricity, and is classed as an amphoteric semiconductor.[8] The volume ratio is

$$\frac{MoO_2}{Mo} = 2.1 \qquad ,$$

as compared with a volume ratio for $MoO_3$ of

$$\frac{MoO_3}{Mo} = 3.3 \qquad .$$

$MoO_2$ can be reduced by hydrogen to the metal at 500°C,[*] and will react with chlorine gas above 600°C to form $MoO_2Cl_2$.

We shall first attempt to consider the mechanism of its formation and then the methods for the removal of the $MoO_2$ film.

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[*]This would seem to be in error, but is the value given by Durrant & Durrant.

If we start by assuming that a layer of $MoO_2$ which is 10 to 100 molecular layers thick exists on the molybdenum surface, it is of some interest to theorize about the fate of newly arriving $O_2$ and HCl molecules. Even for mixtures of HCl and oxygen gases at pressures of 0.1 to 1 torr, there is only a finite probability of the simultaneous arrival of HCl and $O_2$ at the same reaction site. There is also a finite probability that a molecule of $MoO_3$, once formed on the surface of the $MoO_2$ crystal structure, will dissociate and the O atoms formed will either leave the surface or move away from the surface by diffusion before an HCl molecule has arrived. For this reason, and others, a certain portion of arriving HCl and $O_2$ molecules will not react and will be lost. Therefore, it may be seen that if the rate of dissociation of $MoO_3$ at the surface and the diffusion of an oxygen atom away from the surface of the $MoO_2$ lattice is of the same order of magnitude as the rate of arrival of HCl molecules at active sites, then an increase in the partial pressure of either HCl or oxygen will increase the probability of formation of $MoO_2Cl_2$ molecules.

Eventually, under any fixed conditions of gas pressure, gas composition, and substrate temperature, an equilibrium will be established between the rate of growth of the oxide film and the rate of removal of $MoO_3$ by formation of $MoO_2Cl_2$.

It has, in fact, been observed that increasing the quantity of either HCl or $O_2$ increases the rate of removal of molybdenum. This would not be so if we were concerned only with achieving stoichiometry. Some data is given in Fig. 8.

It has also been observed that the etch rate increases very sharply with increased pressure. This is also observed for the oxidation of molybdenum.[11],[12] The mechanism described above could be the explanation for both of the observed effects.

It has further been found that for a given gas mixture there is a certain temperature where the oxide film appears to have a minimum thickness and the etch rate is at a maximum. At temperatures either higher or lower than this critical temperature, the oxide film is found
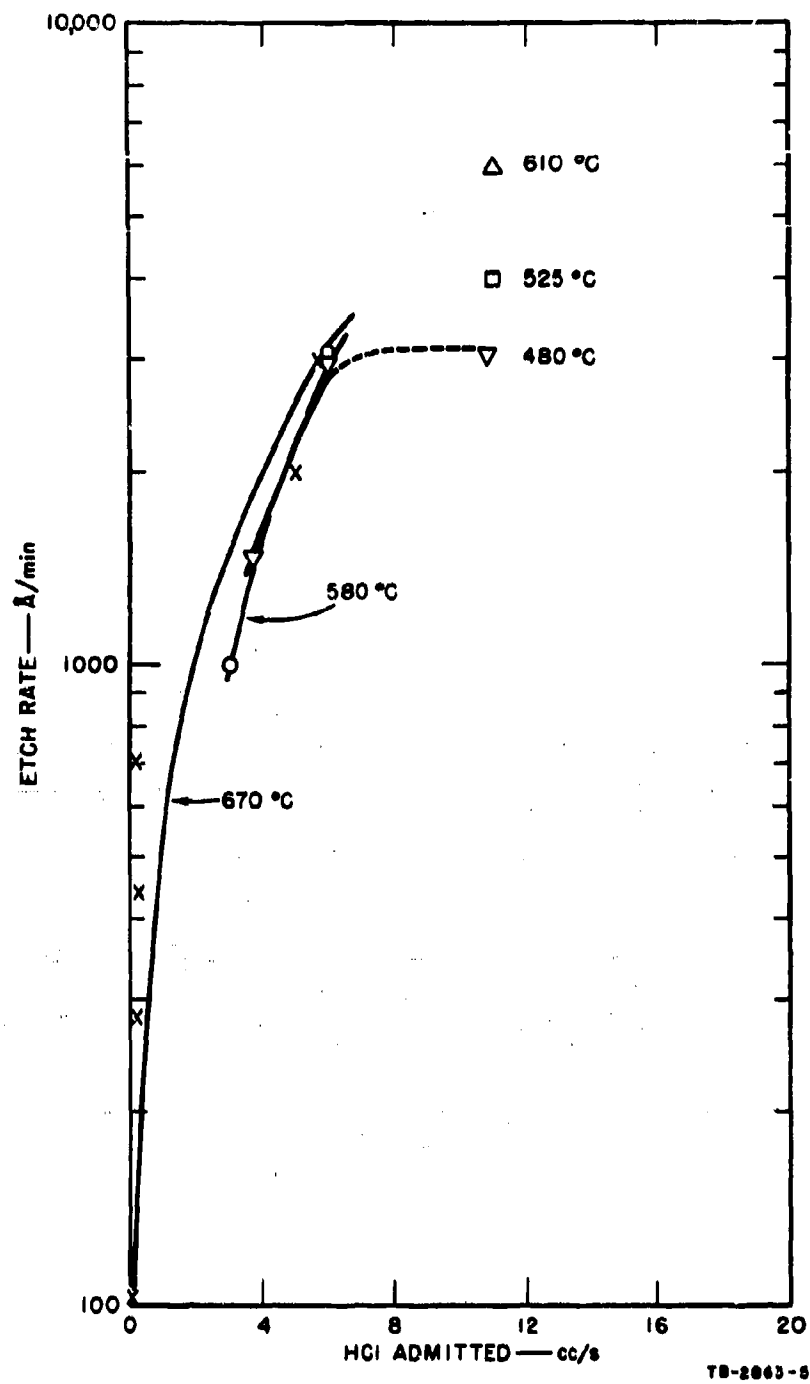
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FIG. 8  ETCH RATE AS FUNCTIONS OF GAS COMPOSITION
FOR VARIOUS SUBSTRATE TEMPERATURES

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and the etch rate is lower. The critical temperature must be that temperature at which the reaction, dissociation, and diffusion rates are balanced to give the most efficient etching. An increase in oxygen pressure was observed to move this band of maximum etch rate to a region of lower temperature on the substrate and an increase in HCl pressure moved the band of maximum etch rate to a region of higher temperature.

As discussed in another section of this report, it may be desirable to maintain a relatively thick oxide layer during etching, and remove it at the end of etching.

Removal of the oxide can be done fairly effectively by firing the film in hydrogen, but the residue of molybdenum metal could be objectionable because of its structure or texture. The oxide film could also be removed by admitting a controlled amount of chlorine gas and heating the substrate to at least $600^{\circ}C$. It has been found, however, that chlorine attacks molybdenum very rapidly under these conditions and may leave an even more undesirable residue of $Mo_6O_{12}$, which is described as a "yellow infusible nonvolatile solid."

The most attractive method of removal of the $MoO_2$ would seem to be by reducing the substrate temperature and increasing the pressure of reactive gases so that surface reaction rates are temporarily favored over dissociation and diffusion rates. The use of atomic or ionic oxygen may have a favorable effect on this problem by increasing the rate of reaction at the surface and thereby increasing the probability of the formation of the oxychloride.

E.   Effects of the Oxide Film

One of the distinguishing characteristics of an etching method is whether or not it tends to roughen, smooth, or brighten a surface. Smoothing and brightening (at least in aqueous processes) both seem to require that a viscous layer or surface film be present over the dissolving surface. The rate at which the reagents reach the reaction zone at the surface of the solid is controlled by diffusion through the surface films;[14] without this rate-controlling film, etch patterns and etch

pits develop as a result of unequal rates of solution of the solid crystals depending upon orientation, imperfections, and impurity sites.

The oxide film which is observed after etching molybdenum in oxygen and hydrogen chloride seems to contribute to a brightening and possibly a smoothing action on molybdenum films, and the presence of the oxide film on molybdenum can and probably does have an effect on the shape of etched holes. The small notch which is seen at the bottom of the hole in sample 49 [Fig. 4(g)] is probably a result of an increase in the concentration gradient of oxygen in that region caused by the insolubility of oxygen in the sapphire, hence an increase in the rate of molybdenum removal from that small area nearest the substrate.

Generally, in polishing type processes, it can be assumed that if an oxide film is present and if its formation is diffusion-limited, a convex surface will be removed more rapidly than a concave surface because of the difference in the surface-to-volume ratio between the two shapes. The degree of this effect will depend upon the thickness of the oxide layer and the radius of curvature of the surface.

## VI  CONCLUSIONS AND RECOMMENDATIONS

A method for high-resolution etching of molybdenum using a mixture of oxygen and hydrogen chloride gases has been developed to the point where it can be evaluated and compared with other etching techniques. Reasonably well controlled and reproducible etching has been done under a range of conditions of temperature, pressure, and gas composition, and etch rates from less than 0.1 $\mu$/min to 1 $\mu$/min and etch factors of 2 or better have been typical for the conditions tried. Pressures from 0.3 to 1 torr have been required to achieve significant etch rates with substrate temperatures between $400^\circ$ and $650^\circ$C.

It has been found that the characteristics of this etching method depend to a great extent upon the mechanism and rate of formation of the molybdenum oxides. Prediction of optimum conditions of temperature and pressure and gas composition for the most rapid etching or for the highest etch factor is difficult, as yet, because the oxidation processes are not adquately understood.

One problem, that cf removal of an oxide film ($MoO_2$) from partially etched surfaces, still exists. This film, although relatively stable and thin, would be objectionable in most circumstances; means of removal should be demonstrated before the process can be used in production of thin-film structures.

The process described in this report has the advantages that the rate and characteristics of etching can be accurately controlled and the etch factor, smoothness of the etched surface, and uniformity in etch rate over a substrate surface have been better than for either the chemical or the electrolytic processes which have been previously tried. Cther techniques, such as sputtering, may offer significant advantages over the oxychloride process, but no direct comparison has been made.

If the problem of removal of the oxide film after etching can be solved, and if a more complete understanding of the oxide formation and

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its removal during etching is developed, the process should be one of the best means of high-precision etching of molybdenum presently available.

Several possibilities of improving the process, including the use of ionized or dissociated oxygen and irradiation of the specimen surface by slow electrons (possibly generated by an RF discharge) have been suggested.

Analysis of the gases present in the reaction chamber could be of some help in confirming present ideas of the overall mechanism. Methods of obtaining a better vacuum environment should also be considered.

# Appendix

## SUMMARY OF RATES OF ETCHING USING VARIOUS COMPOUNDS
## OTHER THAN $O_2$ AND HCl

1. **Pure Dry HCl**

   At 0.5 torr HCl, 800°C, no measurable effect in 3 minutes. Some discoloration but no measurable removal of molybdenum at 1 torr HCl, 700°C in 13 minutes or at 0.6 torr HCl, 650° in 5 minutes.

2. **Pure $Cl_2$**

   Instantaneous removal of 1 to 2μ of molybdenum at 750°C and about 0.2 torr $Cl_2$. At 500°C and 0.1 to 0.2 torr $Cl_2$, holes from 1/4μ openings in $Al_2O_3$ resist were very rough, irregular, and badly undercut. The rate of etching was about 3 μ/min with these conditions.

3. **$O_2$ and $CCl_4$ (Gas)**

   No etching apparent at 200° to 600°C, 0.1 to 0.5 torr each or both of $CCl_4$ and $O_2$. Pump oil was contaminated by $CCl_4$ and required about a day to recover.

4. **$CCl_4$ (Gas)**

   W. Hanson reported severe attack on molybdenum through pinholes in $Al_2O_3$ at 900°C, 0.3 torr, and some attack at 800°C, 0.3 torr.

5. **$H_2O_2$ (Liquid)**

   A 25-percent solution of 30-percent $H_2O_2$ converted a 1000Å film of molybdenum to transparent crystalline oxide in less than 1 minute. Holes etched through 1/4μ openings in $Al_2O_3$ in 1-1/2μ thick molybdenum were extremely irregular. Crystal structure in exposed molybdenum and hole shape showed some directional effects, i.e., holes were more like parallel slits oriented in the same pattern as the larger oxide crystals which grew on the exposed molybdenum.

6. Pure $O_2$

    700 Å/min of molybdenum converted to transparent oxide or partially removed at 700°C, 1 torr $O_2$; 500 Å/min at 670°C, 0.5 torr $O_2$. Oxide residue is usually seen on surface of substrate and on remaining molybdenum films.

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**13. ABSTRACT**

Reactions which lead to the solution or volatilization of molybdenum and which are suitable for high-precision etching of patterns in thin films of molybdenum are not well known. In a search for a process for etching cavities in films 1$\mu$ thick it has been found that the formation and simultaneous removal of molybdenum trioxide can be achieved by exposure of heated molybdenum films to a mixture of oxygen and hydrogen chloride gases. Etch rates of 1000 to 10,000 Å/min have been obtained with specimen temperatures of 400° to 600°C and with gas pressures between 0.1 and 1 torr. An etch factor of about 2 has been typical, and the final etched surface has been as smooth if not smoother than the original surface. Aluminum oxide of about 0.1$\mu$ thickness has been used as a resist. It is hoped that an electron-exposed organic resist can eventually be adapted for use with this process. Discussion and speculation on the mechanism of formation of the oxide and its removal have been included, as well as discussion of some of the factors which are important in predicting the optimum conditions for etching.

A residue of a very thin, adherent layer of $MoO_2$ on partially etched molybdenum surfaces has been a problem, and means for removing this film are discussed. The process appears to have promise for etching with dimensional control accurate to better than 0.1$\mu$ in films 1$\mu$ thick. Greater precision may be possible in films thinner than 1$\mu$.

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